INFLUENCE OF HYDROLYSIS ON PYROLYSIS PRODUCTS FROM SEWAGE SLUDGE

by

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In this research endeavor, the influence of thermal hydrolysis treatment on product distribution obtained through the pyrolysis of hydrolysis treated sludge and raw sewage sludge was investigated. Raw sewage sludge sample was received from a municipal sewage sludge treatment plant, and hydrolysis of sewage sludge was performed at a temperature of 200 °C and a pressure of 0.4 MPa in a fixed-bed furnace. The pore structure of the obtained biochar and non-condensable gas collected at various temperatures was analyzed via Brunauer, Emmett, and Teller and gas chromatography techniques, respectively. The results revealed that thermal hydrolysis treatment had a significant impact on product distribution at varying temperatures (500-800 °C). An increase in temperature led to a decrease in the biochar and biooil yield, while the yield of gas increased for both hydrolysis treated sludge and raw sewage sludge. It was observed that the concentration of H_2, CH_4, and CO from hydrolysis treated sludge was higher than raw sewage sludge. Furthermore, it was observed that by increasing the temperature, the pore volume and specific surface area of the biochar increased while the average pore width decreased. The maximum Brunauer, Emmett, and Teller surface area was measured from biochar obtained from hydrolysis treated sludge at 800 °C as 50.61 m^2/g. The findings suggest that thermal hydrolysis treatment is a viable method for the treatment of sewage sludge as compared to conventional methods.

Key words*: thermal hydrolysis treatment, biochar, sewage sludge, pyrolysis, surface area*

Introduction

As a result of rapid urbanization and industrialization, sewage sludge (SS) management and production pose critical issues faced by society [1, 2]. The SS contains various hazardous substances, including heavy metals, organic matter, pathogenic microorganisms, and harmful inorganic contaminants. If not addressed properly, it may lead to significant threats related to health issues and serious environmental pollution risks [3, 4]. The increase in adverse effects and strict rules in place for SS management has led to the focus on the various energy-related products that can be extracted [5, 6].

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Thus, various sludge pre-treatment technologies, such as mechanical, thermal, biological, and chemical, have been practiced to enhance SS degradation and biogas production [7, 8]. Among them, thermal hydrolysis treatment (THT) has been proposed as an emerging drying method to eliminate most of the moisture content [9, 10]. Furthermore, employing THT for SS before anaerobic digestion (AD) leads to decreased retention time as well as the mass of SS and improves methane generation [11]. The Cambi process is a common thermal hydrolysis method for treating SS and a viable alternative in various conditions. It has been reported to produce value-added products from SS with minimum odor-related concerns, and handling is much less expensive [12].

Several previous studies indicated that THT and pyrolysis are environmentally friendly techniques that reduce the toxicity of the heavy metals in biochar [13]. Most of these studies have investigated the effects of THT on water removal from sludge, improving gas production, and the subsequent AD efficiency by comparing the treated sludge with raw sludge under high temperatures [14]. However, the impact of hydrolysis-treated sludge (HTS) at different temperatures on the pyrolysis product yield and the structure of the obtained biochar remains to be studied. The main purpose of this study is to analyze the pyrolysis effect of raw sewage sludge (RSS) and HTS on the physical properties of biochar, pyrolysis product yield, and composition of gases under different pyrolysis temperatures (500-800 °C).

Experimental

Materials

The materials used for this study were RSS and HTS. The samples were obtained for experiments from a municipal sewage sludge (MSS) treatment plant in Jiangsu, China. The SS was initially treated at a temperature of 200 °C in a reactor with a pressure of 0.4 MPa and a holding period of 30 minutes. The reactor was allowed to cool down and depressurized once the holding time was reached. The samples were obtained from the reactor and stored for further analysis. Before experiments, the RSS and HTS had initially a moisture content of 85% and 13% (*i.e.*, air-dried basis), respectively. After drying in an oven at 105 ±5 °C for 24 hours. Finally, the dried pulverized samples were crushed and sieved through 0.25 mm mesh. The results of proximate and ultimate analysis for the HTS and RSS are presented in tab. 1. The air-dried samples were further analyzed via energy-dispersed X-ray microanalysis (EDXA) as presented in tab. 2 where inorganic elements were determined.

Facilities and procedures

A schematic diagram of the experimental set-up is depicted in fig. 1, where the temperature ranged from 500-800 °C.

Prior to heating, an inert ambiance was created by flowing nitrogen gas at a flow rate of 100 ml per minute for 20 minutes into the specified reactor chamber. The experiment was performed by placing a dried sludge sample of 10.0 g on a crucible boat and placing it into a dehydrator at the required temperature. A heating rate of 10 °C per minute was set and held for an hour to ensure proper drying of the placed samples. The volatile components (*i.e.*, products) were then given passage to a condenser of two bottles in series, surrounded by ice water. Once the residence time was completed, samples were allowed to cool down in the inert environment by shutting off the reactor and the heating rate. The volatiles (*i.e.*, biooil) obtained in the form of liquid from the condensers were stored for further processing. The gaseous products (*i.e.*, mainly about H_2, CO, CO_2, and CH_4) were obtained in a gas bag that was connected after the condenser. Non-condensable gases collected in the gasbags

Table 1. Proximate and ultimate analysis of HTS and RSS

Properties	RSS	HTS
Proximate analysis*		
Ash	59.91 ±0.43	65.83 ±0.18
Moisture	6.95 ±0.14	5.45 ±0.10
Fixed carbon	4.19 ±0.01	2.81 ±0.09
Volatile	28.95 ±0.52	25.91 ±0.23
Ultimate analysis*		
H	5.06 ±0.26	5.46 ±0.14
C	46.48 ±0.54	45.67 ±0.17
O	40.12 ±0.55	39.61 ±0.26
N	5.25 ±0.40	5.05 ±0.24
S	3.09 ±0.19	4.21 ±0.10
Calorific value [$MJkg^{-1}$]*		
LHV	6.03 ±0.4	5.09 ±0.51
Mineral matters*		
SiO_2	43.75 ±0.10	36.24 ±0.05
Al_2O_3	23.82 ±0.15	23.11 ±0.04
P_2O_5	8.64 ±0.14	9.25 ±0.02
Fe_2O_3	8.76 ±0.06	13.55 ±0.09
CaO	4.71 ±0.05	7.30 ±0.05
SO_3	4.0 ±0.07	7.16 ±0.03
K_2O	2.32 ±0.10	1.74 ±0.02
MgO	2.24 ±0.04	1.62 ±0.04
Na_2O	1.66 ±0.07	0.75 ±0.02

*Air-dried basis, wt.%

Table 2. Elemental analysis of RSS and HTS

Samples	Inorganic elements								
	Na	Al	Fe	Si	Mg	K	Ca	S	P
RSS*	1.6 ±0.03	22.1 ±0.02	11.1 ±0.04	41.0 ±0.01	2.1 ±0.01	4.1 ±0.02	6.7 ±0.01	3.5 ±0.01	7.8 ±0.01
HTS*	1.2 ±0.02	21.2 ±0.01	15.7 ±0.03	32.3 ±0.01	1.4 ±0.01	3.2 ±0.03	11.3 ±0.01	5.6 ±0.01	8.1 ±0.01

*Air-dried basis, wt.%

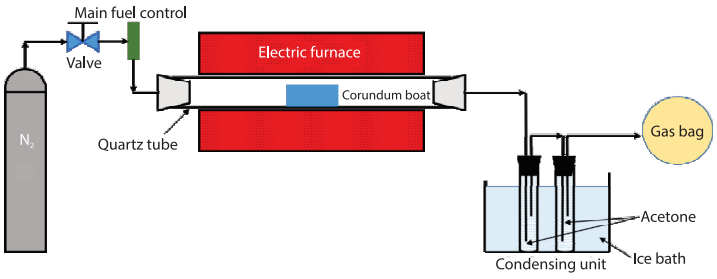

Figure 1. Schematic diagram of a fixed-bed pyrolysis system

were analyzed via gas chromatography (GC). The black solid residue (*i.e.*, biochar) from the pyrolysis process was collected from the previously placed boat and was analyzed and characterized through various techniques. The SS area, pore size, structure, and pore volume of the collected biochar for both HTS and RSS were analyzed by Brunauer, Emmet, and Teller (BET) (ASAP 2020). The experiments were repeated until reproducibility was shown in each case.

Results and discussion

Product analysis

The properties and composition of HTS and RSS samples were investigated through proximate and elementary analysis. The ash compositions are presented in tab. 1. It must be pointed out that the proximate analysis of the HTS sample showed the ash content increased as compared to RSS. In contrast, the volatile and fixed carbon content was reduced due to the loss of volatiles during THT. The results from the ultimate analysis show that the concentration of oxygen and nitrogen in HTS samples was determined to be lower than RSS. This is beneficial as less NO_x is formed, which is detrimental to the environment.

Table 1 depicts that the RSS has relatively higher concentrations of SiO_2 and K_2O, whereas the concentration of CaO content is less than that of HTS. The HTS samples displayed higher amounts of Fe_2O_3, as iron compounds (*i.e.*, $FeCl_3$, $FeSO_4$) are added to SS, which serves as a flocculating species for the collection of particles while drying the SS at the treatment plant [2, 4].

Effect of operating temperature on pyrolysis products

The effect of various temperatures on the yield of the pyrolysis products obtained from 500-800 °C for both HTS and RSS is shown in fig. 2. The pyrolysis experiments were performed three times at the same temperature to ensure reproducible pyrolysis product determinations.

It was observed for both RSS and HTS that the biochar and biooil yield reduced consistently with the increase in operating temperature, which led to the increase in the production of pyrolysis gas. The increase in temperature resulted in decreased biochar and biooil yield, as reported in previous reports [4, 15]. This can be attributed to the fact that at elevated temperatures, large molecules of condensable volatiles are degraded into smaller volatile content, which are non-condensable gases, leading to an increase in gases [16-18]. For RSS, the rise in temperature from 500-800 °C, the biochar and biooil yield decreased from 74.95-68.35% and 12.45-7.55%, respectively. In the same temperature range, the biochar and biooil yield of HTS decreased from 77.8-70.7% and 8.6-4.0%, respectively. At the same time, the gas yield increased from 12.6-24.1% and from 13.6- 25.3% for RSS and HTS, respectively. The differences stated can be linked to more ash content and less volatile contents of the HTS as compared to RSS [19, 20].

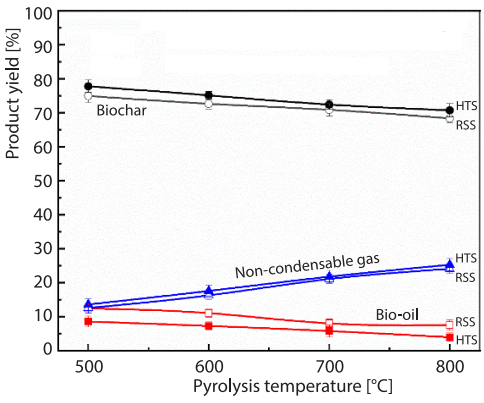

Figure 2. Effect of temperature on product yields for both HTS and RSS

Effect of temperature on the pyrolysis gas composition

The pyrolysis gas composition obtained from 500-800 °C for both HTS and RSS pyrolysis was analyzed through the GC analysis, as depicted in figs. 3(a)-3(d) from the results, it can be seen that the gas was composed mostly of H_2, CH_4, CO, and CO_2. The gas composition and yield differed for both RSS and HTS at the same operating temperatures (*i.e.*, fig. 3).

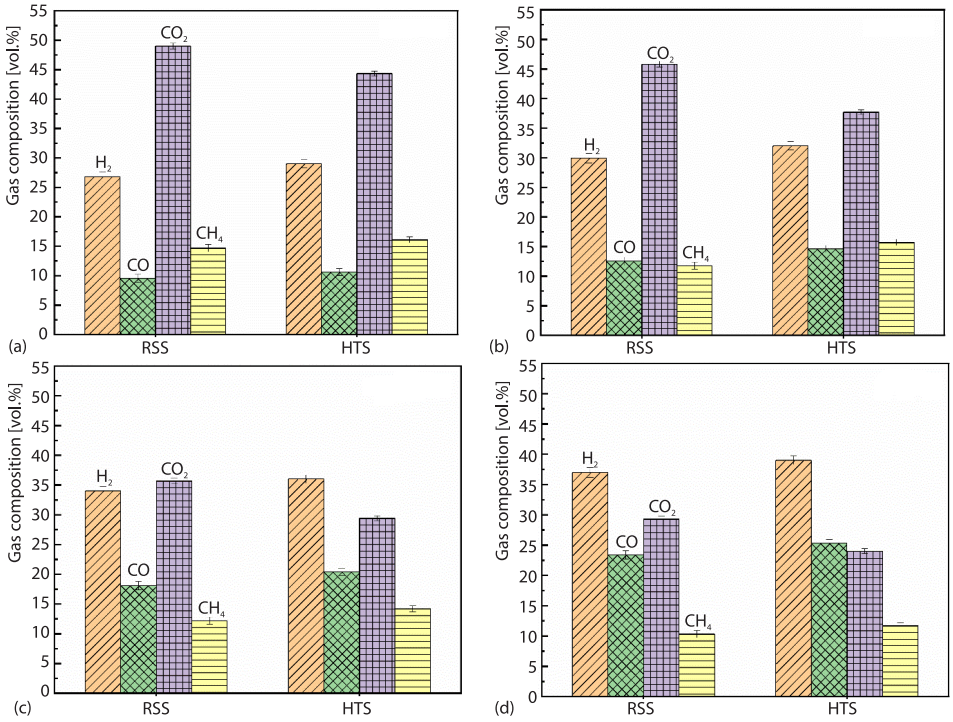

Figure 3. Effect of temperature on the pyrolysis gas composition for both RSS and HTS; (a) 500 °C, (b) 600 °C, (c) 700 °C, and (d) 800 °C

From fig. 3 it can be seen that the yield trend of primary products (CH_4 and H_2) was greatly influenced during the pyrolysis of HTS. Meanwhile, the trend for CO and CO_2 was similar for both RSS and HTS. It shows that as the pyrolysis temperature is elevated, the concentration of CO_2 and CH_4 decreased sharply from 44.3-24% and 16-11%, respectively. However, H_2 and CO contents increased remarkably during the pyrolysis of HTS as compared to RSS. This could be because the organic matter decreases as it is decomposed in HTS samples, hence resulting in less production of CO_2.

Furthermore, it was observed that as temperature increased, the production of CH_4 was decreased. Various studies similarly reported that the amount of CH_4 can be linked to different reactions taking place during pyrolysis [21, 22]. Therefore, THT has an impactful effect on the products formed from sludge pyrolysis, leading to reduced GHG emissions [23, 24].

Biochar surface area under different pyrolysis temperatures

The characteristics of the biochar's porous network resulting from the pyrolysis of HTS and RSS at 600 °C and 800 °C are provided in tab. 3. The results suggest that the increase in operating pyrolysis temperature (*i.e.*, HTS800) facilitated the formation of the mesopores compared to biochar obtained from RSS800.

Table 3. Pore structures of the biochar obtained from the HTS and RSS

Pore structure	Samples			
	RSS600	RSS800	HTS600	HTS800
Surface area [m^2g^{-1}]	36.22	41.49	46.87	50.61
Total pore volume [cm^3g^{-1}]	0.0037	0.0046	0.0034	0.0025
Average pore width [nm]	17.33	16.19	16.27	10.72

When the temperature was elevated (*i.e.*, from 600-800 °C), the biochar displayed enhanced specific surface area and a total pore volume for HTS samples, which increased from 46.87 m^2/g and 0.0034 to 50.61 m^2/g and 0.0025 cm^3/g, respectively. Moreover, the average pore size was observed to decrease from 16.27 nm to 10.72 nm. Lu *et al.* [25] detailed that this reduction in BET surface area of char was a result of the escaping of volatile content when the temperature increased from 550-650 °C along with the occurrence of the sintering processes which take place over 850 °C. This volatilization of the organic matter during the formation of biochar is beneficial in the overall development of the aforementioned porous network [26, 27].

In this study, the biochar obtained from HTS and RSS under various operating temperatures was found to possess a mesoporous structure. Figures 4(a) and 4(b) shows the iso-

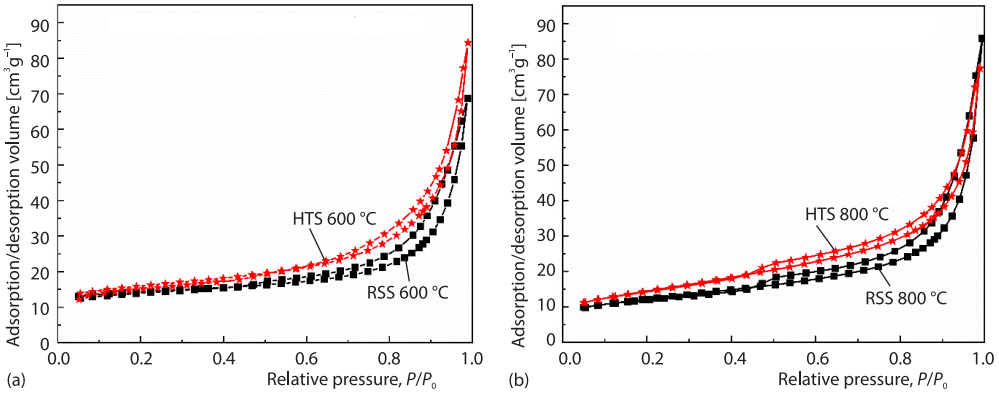

Figure 4. Nitrogen adsorption-desorption isotherms of biochars obtained from HTS and RSS at different pyrolysis temperatures; (a) 500 °C and (b) 800 °C

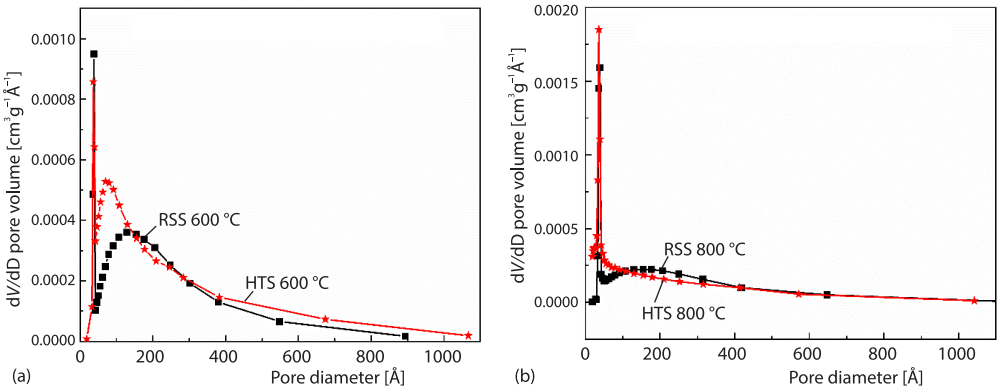

Figure 5. The pore size distribution of biochar obtained from HTS and RSS at different pyrolysis temperatures; (a) 500 °C and (b) 800 °C

therms derived from N_2 adsorption-desorption analysis. The obtained curves represent type IV adsorption isotherms as per the guidelines of IUPAC classification, and the obtained pore size distribution confirms this result. Figures 5(a) and 5(b) displays the distribution of various biochar pore sizes collected from HTS and RSS, which were similar and showed familiar positions of the horizontal peaks.

Conclusion

In this research endeavor, a fixed-bed reactor was utilized to thermally treat and compare the influence of THT on product distribution obtained during the pyrolysis of HTS and RSS under different operating temperatures (*i.e.*, 500-800 °C). The results of this study reveal the increase in pyrolytic temperature resulted in yield reduction of biochar and biooil for both HTS and RSS. On the other hand, the gas yield increases when the operating temperature is raised (*i.e.*, 500-800 °C). It was also observed that the biochar yield of HTS and RSS decreased from 74.95-68.35% and 77.8-70.7%, respectively. Meanwhile, gas yield increases from 12.6-24.1% and from 13.6-25.3% for RSS and HTS, respectively. The concentration of H_2, CH_4, and CO from the pyrolysis of HTS was greater at high temperatures than RSS pyrolysis. Furthermore, the maximum BET surface area determined for biochar of HTS at 800 °C was found to be 50.61 m^2/g. This concludes that THT is a feasible technique to treat sewage sludge to obtain various products. This provides a basis for future studies to be implemented at a large-scale for the valorization of sewage sludge.

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Nomenclature

Acronyms

AD – anaerobic digestion
BET – Brunauer, Emmett, and Teller
EDXA – energy-dispersed X-ray
GC – gas chromatography
HTS – hydrolysis treated sludge
IUPAC – International union of pure and applied chemistry
MFC – main fuel control
MSS – municipal sewage sludge
RSS – raw sewage sludge
SS – sewage sludge
THT – thermal hydrolysis treatment

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